

***trans*-Bis(2-amino-6-nitro-1,3-benzothiazole-*N*)dichloroplatinum(II) tetrakis(*N,N'*-dimethylformamide) solvate and tetrakis(2-amino-5-methyl-1,3,4-thiadiazole-*N*⁴)-platinum(II) hexachloroplatinate(IV) bis(*N,N'*-dimethylformamide) solvate**

Daniel E. Lynch* and Helen L. Duckhouse

School of Science and the Environment, Coventry University, Coventry CV1 5FB, England

Correspondence e-mail: apx106@coventry.ac.uk

Received 5 June 2001

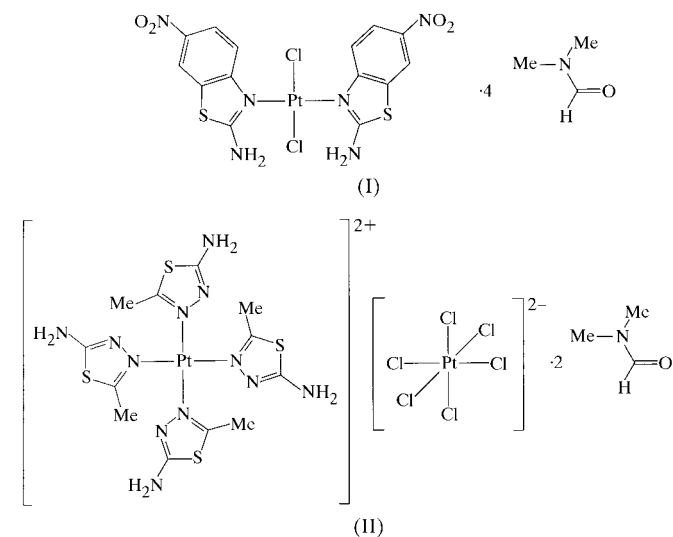
Accepted 15 June 2001

The structures of the title compounds, $[\text{PtCl}_2(\text{C}_7\text{H}_5\text{N}_3\text{O}_2\text{S})_2] \cdot 4\text{C}_3\text{H}_7\text{NO}$, (I), and $[\text{Pt}(\text{C}_3\text{H}_5\text{N}_3\text{S})_4][\text{PtCl}_6] \cdot 2\text{C}_3\text{H}_7\text{NO}$, (II), respectively, comprise square-planar Pt^{II} centres. In the cation and anion of (II), the Pt atoms lie on independent inversion centres. For (I), the metal atom is N-bonded to two *trans* organic ligands and also bonded to two Cl atoms, whereas in (II), the Pt atom is N-bonded to four organic ligands, the charge being balanced by the presence of an additional $[\text{PtCl}_6]^{2-}$ species (from the starting material). Both structures contain dimethylformamide solvate molecules, four in the asymmetric unit of (I) and one in (II), which are involved in the hydrogen-bonding network *via* $\text{N}-\text{H} \cdots \text{X}$ and $\text{C}-\text{H} \cdots \text{X}$ associations.

Comment

The structures of many metal complexes of 2-amino-1,3-thiazole derivatives, where the metal is directly bound to the ligand, are known and include most of the *d*-block first-row transition metals (*i.e.* Mn–Zn), plus a few others (such as Mo, Hg and Cd). In all but a few of these cases, the thiazoles bind to the metal *via* N3. Our current interest in studying the hydrogen-bonding features of 2-amino-1,3-thiazoles has led us to investigate such aspects in their metal complexes, especially when the main hydrogen-bond acceptor atom (N3) is bound to the metal. Interestingly, a Cambridge Structural Database (CSD) search (Fletcher *et al.*, 1996) reveals that there are 13 reported single-crystal structures of 1,3-thiazole complexes with Pt, but none for any 2-amino (*i.e.* NH_2) analogues. However, by mixing chloroplatinic acid with a series of thiazole derivatives, we expected to produce $[\text{bis}(\text{thiazolium})]^{2+}[\text{PtCl}_6]^{2-}$. Several similar complexes of this type with 2-amino-1,3-thiazole derivatives are known and include

anions such as $[\text{CuCl}_4]^{2-}$ (Férez *et al.*, 1996), $[\text{ZnCl}_4]^{2-}$ (Kubiak & Glowiak, 1984), $[\text{Cd}_4\text{Cl}_{11}]^{4-}$, $[\text{BiL}_4]^-$, $[\text{Bi}_2\text{Br}_{10}]^{4-}$ and $[\text{Sb}_4\text{Br}_{16}]^{4-}$. In each of these complexes, $\text{N}-\text{H} \cdots \text{Cl}$ interactions dominate the hydrogen-bond network. Instead, our syntheses yielded the title compounds, (I) and (II), which have Pt coordination to N3 but also contain *N,N'*-dimethylformamide (DMF) solvent molecules that are intricately involved in hydrogen-bond interactions.



The structures of (I) and (II) both contain square-planar Pt^{II} complexes, which is interesting because the platinum from the starting material has undergone reductive elimination. Selected bonds involving Pt for (I) are listed in Table 1, while hydrogen-bond geometries are given in Table 2. In (I), the organic ligands are *trans* across the Pt atom but oriented in the same direction, the charge (and coordination) being balanced by two bound Cl atoms (Fig. 1). The thiazoles are essentially coplanar [dihedral angle $4.5 (1)^\circ$] and are involved with three of the four DMF molecules in strong $\text{N}-\text{H} \cdots \text{O}$ hydrogen-bonding associations from the 2-amino groups (Fig. 2). This packing arrangement may explain the specific orientation of the two thiazoles. Several $\text{C}-\text{H} \cdots \text{O}$ short contacts are also listed in Table 2, with the majority of $\text{C}-\text{H}$ donors being from the *N*-methyl groups of the DMF molecules.

Complex (II) has one Pt^{II} cation species surrounded by four N-bonded organic ligands and one $[\text{PtCl}_6]^{2-}$ anion to balance

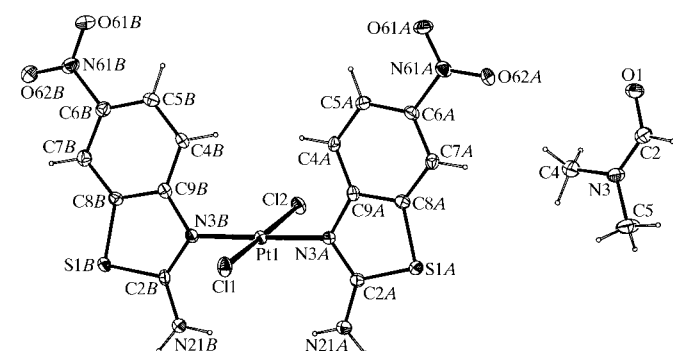


Figure 1
The molecular configuration and atom-numbering scheme for (I), showing 30% probability ellipsoids. Three DMF molecules have been omitted for clarity.

the charge (Fig. 3). Again, the Pt complex has undergone formal reductive elimination, although it is interesting to encounter a mixed-valence system. The cation has two symmetry-unique thiazoles [dihedral angle $89.9 (8)^\circ$], whereas the anion has three crystallographically unique Cl atoms; both Pt centres reside on inversion centres. Complex (II) contains only one DMF molecule in the asymmetric unit and this is involved in hydrogen-bond associations (Table 4), although the majority of hydrogen-bond interactions from the 2-amino

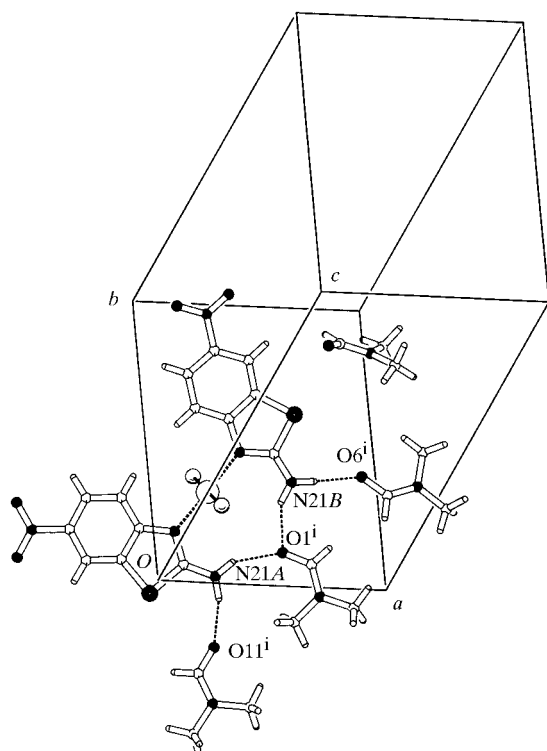


Figure 2
Packing diagram of (I). Hydrogen-bonding interactions are shown as dotted lines. [Symmetry codes: (i) $-x, 1-y, -z$; (ii) $x-1, y, z$.]

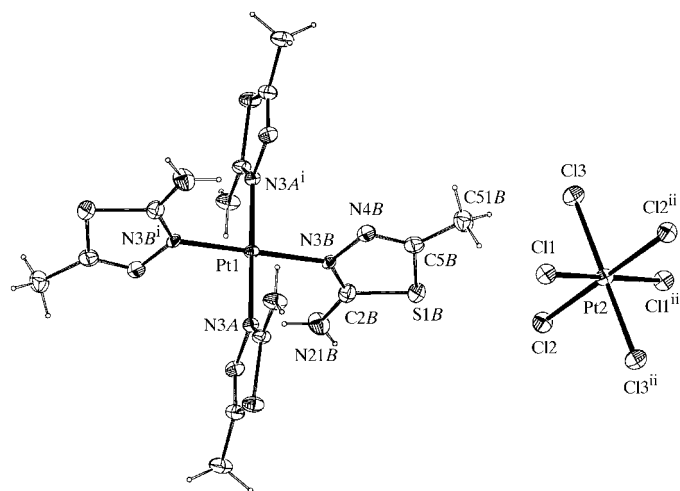


Figure 3
The molecular configuration and atom-numbering scheme for (II), showing 30% probability ellipsoids. The single DMF molecule in the asymmetric unit has been omitted for clarity. [Symmetry codes: (i) $1-x, -y, -z$; (ii) $-x, -1-y, 1-z$.]

H atoms use the chlorides as acceptors (Fig. 4). The DMF molecules reside neatly between the inner-facing 2-amino H atoms; the outer-facing H atoms both associate *via* three-centre interactions to adjacent Cl atoms. The *N*-attachment of the organic ligands in complexes (I) and (II) leaves an outer-facing S atom that is susceptible to close contact from another large atom. In (I), S1B is $3.649 (5) \text{ \AA}$ from a related atom (*i.e.*

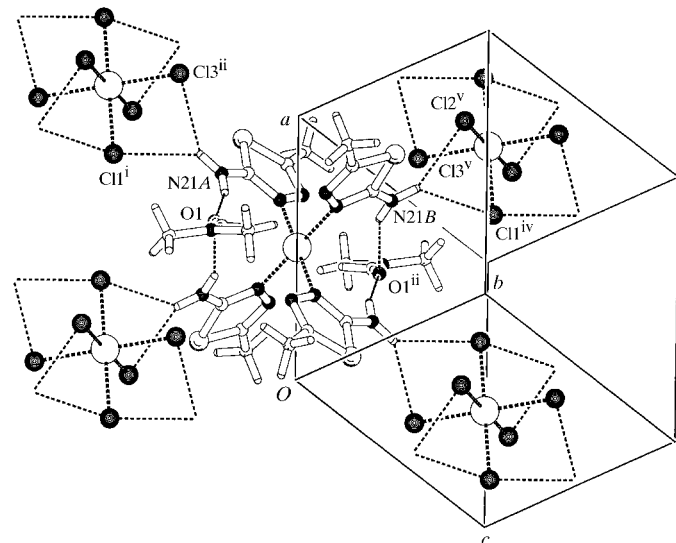


Figure 4
Packing diagram of (II). Hydrogen-bonding interactions are shown as dotted lines. [Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x, 1+y, z$; (iii) $1-x, -y, -z$; (iv) $-x, -1-y, -z$; (v) $x, y, z-1$.]

S1B at $-x, -y, -z$) and is also $3.459 (5) \text{ \AA}$ from Cl1($-x, -y, -z$). S1A is $3.050 (5) \text{ \AA}$ from O16($-x, -y, -z$), while S1B is $3.273 (5) \text{ \AA}$ from O6($-1+x, y, z$). In (II), S1A has the greater number of close contacts and is $3.78 (1) \text{ \AA}$ from S1B($-x, -y, -z$), $3.62 (1) \text{ \AA}$ from Cl1($-x, -y, 1-z$), and $3.58 (1) \text{ \AA}$ from Cl2($x, -1-y, z$), while S1B is $3.54 (1) \text{ \AA}$ from Cl2($-x, -1-y, -z$), while S1B is $3.55 (1) \text{ \AA}$ from Cl1($-x, -y, -z$) in (I) and $3.55 (1) \text{ \AA}$ (symmetry code: $1-x, -y, -z$) in (II).

Experimental

Complexes (I) and (II) were prepared by dissolving (with heating) 1:2 molar amounts of chloroplatinic acid with 2-amino-6-nitro-1,3-benzothiazole for (I) and 2-amino-5-methyl-1,3,4-thiadiazole for (II) in dry DMF. Crystals were separated from the reaction solutions after three weeks.

Compound (I)

Crystal data

[PtCl₂(C₇H₅N₃O₂S)₂]₂·4C₃H₇NO
 $M_r = 948.77$
 Triclinic, *P1*
 $a = 11.137 (2) \text{ \AA}$
 $b = 12.671 (3) \text{ \AA}$
 $c = 14.409 (3) \text{ \AA}$
 $\alpha = 64.28 (3)^\circ$
 $\beta = 85.77 (3)^\circ$
 $\gamma = 78.28 (3)^\circ$
 $V = 1793.4 (6) \text{ \AA}^3$

$Z = 2$
 $D_x = 1.757 \text{ Mg m}^{-3}$
 Mo $K\alpha$ radiation
 Cell parameters from 29 063 reflections
 $\theta = 2.9\text{--}27.5^\circ$
 $\mu = 4.24 \text{ mm}^{-1}$
 $T = 150 (2) \text{ K}$
 Needle, yellow
 $0.28 \times 0.08 \times 0.05 \text{ mm}$

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.389$, $T_{\max} = 0.816$
 29 010 measured reflections
 8177 independent reflections

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.037$
 $wR(F^2) = 0.094$
 $S = 1.04$
 8177 reflections
 451 parameters
 H-atom parameters constrained

Table 1

Selected geometric parameters (\AA , $^\circ$) for (I).

Pt1—Cl1	2.2935 (14)	Pt1—N3A	2.015 (3)
Pt1—Cl2	2.3031 (13)	Pt1—N3B	2.023 (3)
N3A—Pt1—N3B	178.80 (11)	C9A—N3A—Pt1	123.2 (3)
Cl1—Pt1—Cl2	177.75 (3)	C2B—N3B—Pt1	124.8 (3)
C2A—N3A—Pt1	125.5 (3)	C9B—N3B—Pt1	124.0 (3)

Table 2

Hydrogen-bonding and short-contact geometry (\AA , $^\circ$) for (I).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N21A—H21A \cdots O1 ⁱ	0.88	1.98	2.778 (5)	150
N21A—H22A \cdots O11 ⁱ	0.88	1.89	2.765 (6)	175
N21B—H21B \cdots O1 ⁱ	0.88	2.00	2.804 (5)	151
N21B—H22B \cdots O6 ⁱⁱ	0.88	1.94	2.794 (5)	164
C7A—H7A \cdots O16 ⁱⁱⁱ	0.95	2.47	3.212 (6)	135
C17—H17 \cdots O62B ^{iv}	0.95	2.54	3.455 (6)	162
C4—H43 \cdots O1 ^v	0.98	2.47	3.416 (7)	163
C5—H51 \cdots O61A ^{vi}	0.98	2.49	3.050 (6)	116
C9—H93 \cdots O6	0.98	2.37	2.766 (6)	104
C14—H141 \cdots O11	0.98	2.33	2.738 (8)	104
C15—H153 \cdots Cl1 ^{vii}	0.98	2.75	3.675 (5)	158
C20—H203 \cdots O62A ^{viii}	0.98	2.43	3.271 (7)	144

Symmetry codes: (i) $-x, 1-y, -z$; (ii) $x-1, y, z$; (iii) $-x, -y, -z$; (iv) $x, 1+y, z$; (v) $1-x, 2-y, -z$; (vi) $1-x, -y, -z$; (vii) $1-x, 1-y, -z$; (viii) $1+x, 1+y, 1+z$.

Compound (II)

Crystal data

$[\text{Pt}(\text{C}_3\text{H}_5\text{N}_3\text{S}_4)]_4[\text{PtCl}_6] \cdot 2\text{C}_3\text{H}_7\text{NO}$
 $M_r = 1209.70$
 Triclinic, $P\bar{1}$
 $a = 9.0397$ (4) \AA
 $b = 9.3009$ (4) \AA
 $c = 11.5241$ (5) \AA
 $\alpha = 109.027$ (2°)
 $\beta = 91.850$ (3°)
 $\gamma = 91.785$ (3°)
 $V = 914.61$ (7) \AA^3

Data collection

Enraf–Nonius KappaCCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SORTAV; Blessing, 1995)
 $T_{\min} = 0.573$, $T_{\max} = 0.921$
 6735 measured reflections
 3838 independent reflections

$Z = 1$
 $D_x = 2.196$ Mg m^{-3}
 Mo $K\alpha$ radiation
 Cell parameters from 4414 reflections
 $\theta = 2.9\text{--}27.5^\circ$
 $\mu = 8.35$ mm^{-1}
 $T = 150$ (2) K
 Prism, yellow
 $0.08 \times 0.03 \times 0.01$ mm

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.048$
 $wR(F^2) = 0.135$
 $S = 1.07$
 3838 reflections
 216 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0370P)^2 + 8.3603P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 2.38$ e \AA^{-3}
 $\Delta\rho_{\min} = -2.59$ e \AA^{-3}
 Extinction correction: SHELXL97
 Extinction coefficient: 0.0032 (6)

Table 3

Selected bond lengths (\AA) for (II).

Pt2—Cl1	2.320 (3)	Pt1—N3A	2.019 (7)
Pt2—Cl2	2.317 (3)	Pt1—N3B	2.037 (7)
Pt2—Cl3	2.323 (3)		

Table 4

Hydrogen-bonding and short-contact geometry (\AA , $^\circ$) for (II).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N21A—H21A \cdots O1	0.88	1.98	2.816 (12)	158
N21A—H22A \cdots CH ⁱ	0.88	2.62	3.389 (9)	146
N21A—H22A \cdots Cl3 ⁱⁱ	0.88	2.72	3.430 (10)	139
N21B—H21B \cdots O1 ⁱⁱⁱ	0.88	2.04	2.849 (14)	153
N21B—H22B \cdots Cl2 ^{iv}	0.88	2.61	3.399 (12)	150
N21B—H22B \cdots Cl3 ^v	0.88	2.82	3.516 (10)	137
N21B—H22B \cdots Cl1 ^v	0.88	2.91	3.341 (10)	112
C4—H41 \cdots Cl1 ^{vi}	0.98	2.82	3.44 (2)	122

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $x, 1+y, z$; (iii) $1-x, -y, -z$; (iv) $-x, -1-y, -z$; (v) $x, y, z-1$; (vi) $1-x, -y, 1-z$.

All H atoms were included in the refinement at calculated positions as riding models, with C—H distances set to either 0.98 (CH₃) or 0.95 \AA (CHO) and the N—H distance set to 0.88 \AA .

For both compounds, data collection: DENZO (Otwinowski & Minor, 1997) and COLLECT (Hooft, 1998); cell refinement: DENZO and COLLECT; data reduction: DENZO and COLLECT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: PLATON97 (Spek, 1997); software used to prepare material for publication: SHELXL97.

The authors acknowledge financial support from the School of Science and the Environment (Coventry) and thank the EPSRC National Crystallography Service (Southampton) and the Chemical Database Service of the EPSRC at Daresbury.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GG1066). Services for accessing these data are described at the back of the journal.

References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–37.
 Fernández, V., Doadrio, J. C., Garcia-Granda, S. & Perterra, P. (1996). *Acta Cryst.* **C52**, 1412–1415.
 Fletcher, D. A., McMeeking, R. F. & Parkin, D. (1996). *J. Chem. Inf. Comput. Sci.* **36**, 746–749.
 Hooft, R. (1998). COLLECT. Nonius BV, Delft, The Netherlands.
 Kubiak, M. & Glowiak, T. (1984). *Acta Cryst.* **C40**, 2039–2041.
 Otwinowski, Z. & Minor, W. (1997). *Methods Enzymol.* **276**, 307–326.
 Sheldrick, G. M. (1997). SHELXS97 and SHELXL97. University of Göttingen, Germany.
 Spek, A. L. (1997). PLATON97. University of Utrecht, The Netherlands.